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AIRCRAFT EQUIPMENT DIVISION

REPORT

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INVESTIGATION OF BROMINE COMPLEXED HYDROGEN/BROMINE REGENERATIVE FUEL CELLS FOR PORTABLE ELECTRIC POWER

MERADCOM Contract No. DAAK 70-82-C-0088

FINAL REPORT

J. A. Kosek and A. B. LaConti

Prepared for:

U.S. Army Mobility Equipment Research
and Development Command
Fort Belvoir, VA 22060

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1.0

INTRODUCTION

A bromine storage system based on the formation of a complex between polyethylene glycol (PEG) (1000 MW) and bromine has been developed. This bromine storage system, developed initially under General Electric funding (1,2) and optimized under funding from the U.S. Army (MERADCOM), has been developed for use in an SPE[®] hydrogen/bromine regenerative fuel cell system.

The electrochemical reactions for the hydrogen/bromine cycle are displayed in Figure 1. During charge, hydrogen bromide is electrolyzed into hydrogen and bromine. These fluids are then stored separately outside the electrochemical cell. (Since all reactants are stored external from the cell, independent sizing for power and energy storage becomes a distinct advantage.) During discharge, the hydrogen and bromine are delivered to the cell, where they react electrochemically to produce electric power and hydrogen bromide.

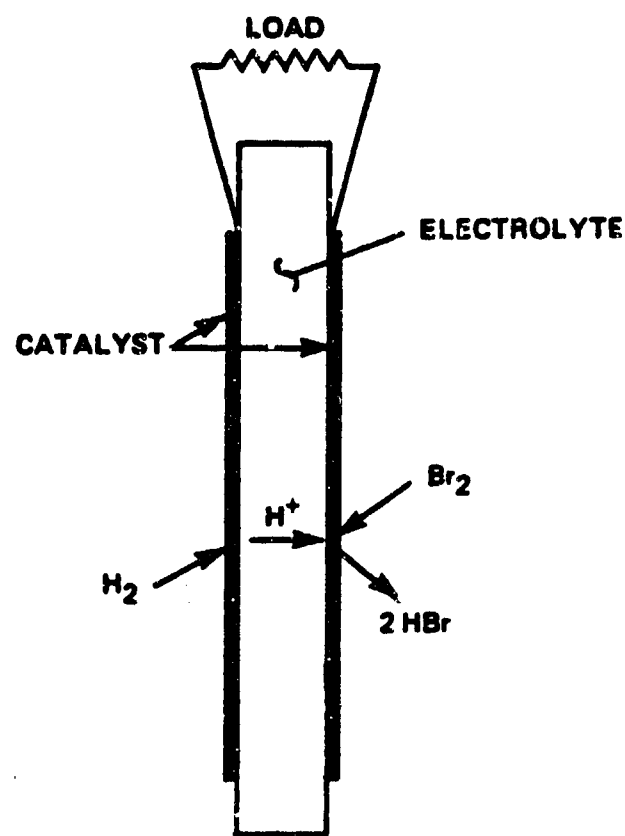
The quantity of elemental bromine available in the system inventory establishes the discharge capacity of the positive electrode in an H₂/Br₂ fuel cell battery. A large mass of bromine is ordinarily desirable in order to maximize the overall battery capacity. Perhaps the simplest method to achieve this is to operate at bromine saturation, maintaining the bromine inventory as the liquid element.

Bromine, however, is a volatile liquid, boiling at 59°C. For a number of practical reasons, it is desirable to reduce the halogen vapor pressure in an energy storage system. In the event of an equipment malfunction involving a liquid spill, cleanup and worker hygiene are simplified if bromine remains in a condensed phase. Materials problems are simplified if the activity of bromine in solution is held below its saturation value.

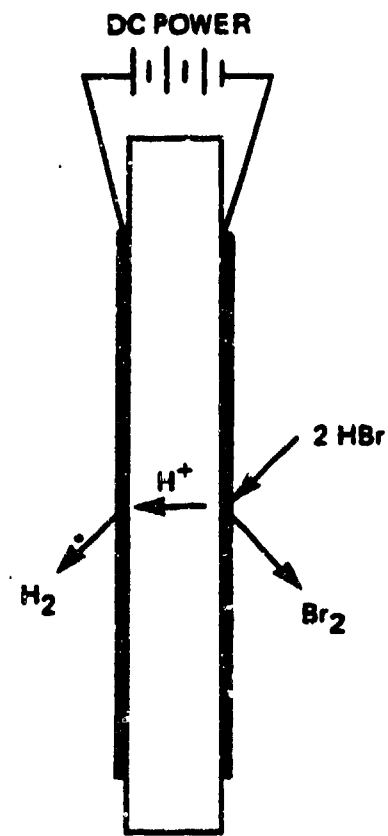
The bromine-storage system was developed for the sole purpose of reducing the halogen vapor pressure. The principle of operation is as follows: During the charge (electrolysis) cycle, bromine liberated at the positive electrode reacts with PEG dissolved in HBr to form a complex:



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HYDROGEN BROMINE
FUEL CELL
(DISCHARGE)



HYDROBROMIC
ACID
ELECTROLYSIS
(CHARGE)

Figure 1. Hydrogen/Bromine Regenerative Fuel Cell Cycle

The activity of free bromine is then determined by the formation constant of the complex. During discharge (fuel cell operation) bromine is consumed from solution and the complex dissociates:



to provide the halogen as it is required.

Phase I of this program, described in an uncirculated Interim Report(3), evaluated some of the physical/chemical properties of the PEG-Br₂ complex. This complex has the form of a viscous, red oil. It was determined the most favorable conditions for complex formation/bromine capacity were ~3M HBr at or near room temperature. This report completes the characterization study of the complex by measuring rate constants for the dissociation of the complex. Phases II and III of this program involved optimization of the fuel cell bromine electrode and actual operation of the fuel cell using bromine supplied by the PEG-Br₂ complex. Significant results obtained during Phase I of the program are summarized in Appendix I.

2.0 INVESTIGATION OF THE POLYETHYLENE GLYCOL/BROMINE STORAGE SYSTEM

2.1 Kinetics of Complex Dissociation

Fuel cell performance can be related to the concentration of bromine at the cathode surface. Therefore, to effectively utilize a bromine complexing system such as PEG-1000, the complex must be able to rapidly dissociate and provide free bromine to the electrode surface.

Kinetic studies were conducted using 1-5M HBr as a reaction medium, and over the temperature range 24-43°C. The rate constants, summarized in Table I, were measured using the electrochemical technique of chronopotentiometry in a thermostated cell. A platinum sensing electrode was immersed directly into a stagnant pool of oil located in the bottom of the electrochemical cell. The oil was stirred after each run by means of a stir bar and magnetic stirrer.

At a given temperature, the largest value for the dissociation rate constants were observed in 3M HBr. Also, as the temperature increased, the value of the rate constant decreased. This meant the most rapid complex dissociation was observed in 3M HBr at room temperature.

TABLE I

PEG-Br₂ COMPLEX DISSOCIATION RATE CONSTANTS

<u>HBr CONC.</u>	<u>24°C</u>	<u>34°C</u>	<u>43°C</u>
<u>1M</u>	6.25 sec ⁻¹	0.06 sec ⁻¹	-
<u>3M</u>	51.02 sec ⁻¹	0.12 sec ⁻¹	0.12 sec ⁻¹
<u>5M</u>	4.20 sec ⁻¹	0.05 sec ⁻¹	0.04 sec ⁻¹

To verify that the electrode was responding to complexed bromine, an experiment was conducted using only bromine in 3M HBr; no PEG was present. Bromine concentrations were set relatively close to that of the bromine complexed with PEC (0.016 Vs. 0.021M).

Values of $i_0\tau^{1/2}$ (the "chronopotentiometric constant") for the system without PEG present were over an order of magnitude smaller than for a comparable experiment with glycol present. The quantity $i_0\tau^{1/2}$ is dependent only on the applied current density (i_0) and the transition time (τ) of the system. For a reaction which involves a chemical step preceding the electrochemical reaction, the transition time will be longer (at constant current density) than for a reaction which does not involve a preceding chemical reaction. To keep the transition times in the above experiments reasonable for accurate measurement, the current density of the bromine-only experiment was lowered one-to-two orders of magnitude from those used in the PEG experiments. The large difference in applied current densities indicated the electrochemical reaction in the absence of PEG was proceeding at a much more rapid rate than with PEG present.

2.2 Electrode Development

Another goal of this program was optimization of the bromine electrode, for efficient fuel cell operation. Efforts were directed initially toward the optimization of the electrode for use with bromine only; the optimized electrode, and similar configurations, were then evaluated with the PEG-Br₂ complex.

A baseline H₂/Br₂ SPE fuel cell was constructed using platinized components on the bromine side, and a platinum catalyst. Performance of this fuel cell is shown in Figure 2. The performance plot presented in Figure 2 was considered baseline performance and was the standard against which all other fuel cell performance was measured.

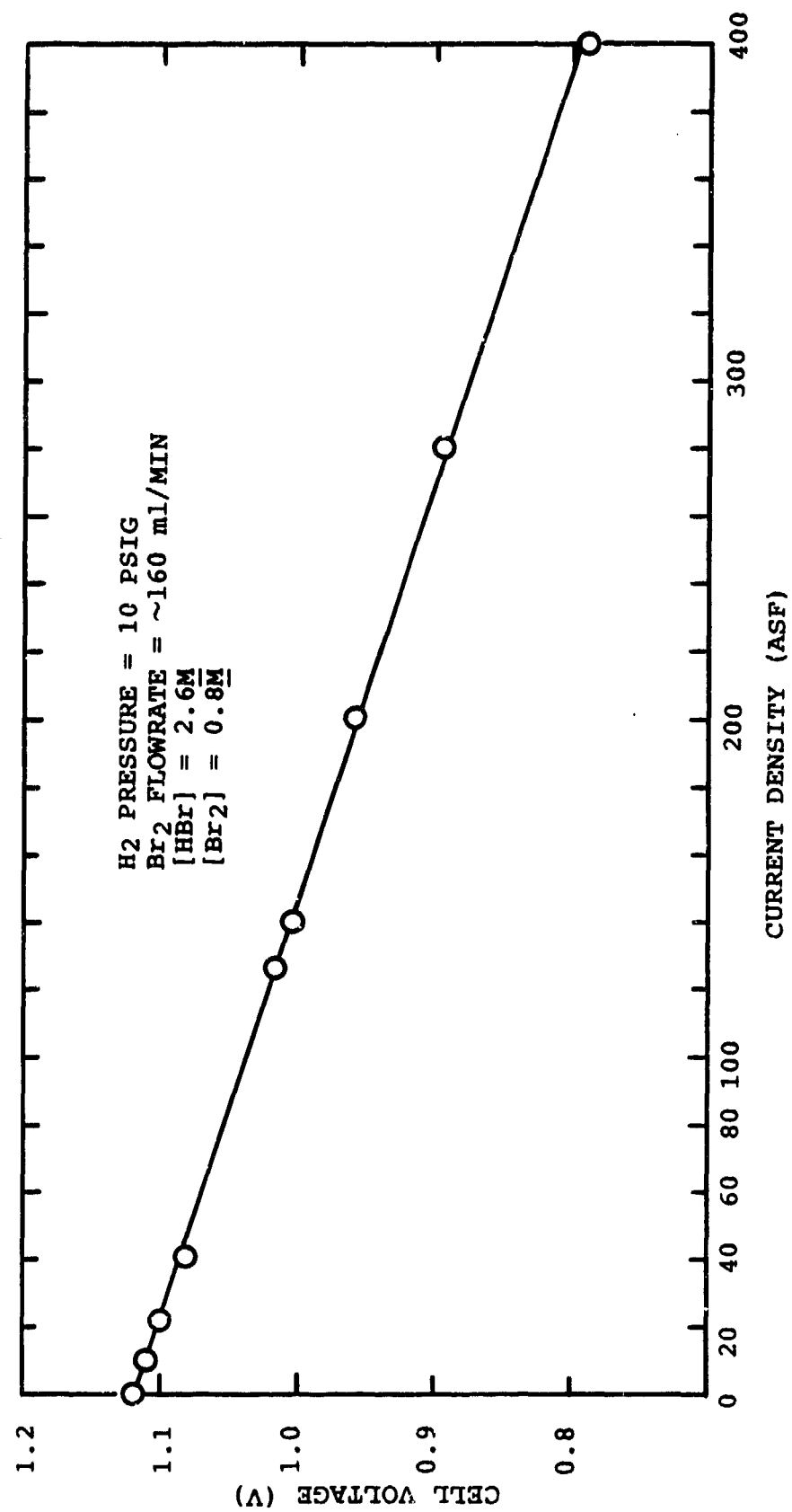


Figure 2. Baseline H₂/Br₂ Fuel Cell Performance

One serious disadvantage to the use of platinized components in a Br₂/HBr environment was the potential for dissolution of the platinum located both in the catalyst and plated on the surface of the fuel cell components. Dissolution of the Pt catalyst was observed in several instances. Figure 3 demonstrates fuel cell performance for several alternative cathode catalysts. Catalysts evaluated included a heat-stabilized Ru/Ir mixture, Ir, a Pt/Ir mixture and graphite.

Table II compares the performance of the five cathode catalysts evaluated. The highest voltage (at 300 ASF) was observed for the baseline system. The next group of catalysts, all containing Ir, exhibited similar performance. Finally, a large drop was observed going to graphite.

TABLE II
RELATIVE PERFORMANCE, VARIOUS CATHODE CATALYSTS

<u>CATALYST</u>	<u>VOLTAGE AT 300 ASF</u>	<u>SLOPE</u>	<u>CALCULATED RESISTANCE</u>
Pt	0.875V	80 mV/100 ASF	16 mΩ
Pt-Ir	0.825V	86 mV/100 ASF	17 mΩ
Ru-Ir	0.815V	95 mV/100 ASF	19 mΩ
Ir	0.805V	95 mV/100 ASF	19 mΩ
Graphite	0.730V	115 mV/100 ASF	23 mΩ

Also shown in Table II are the slopes of the polarization curves shown in Figure 3, and the resistances calculated from these slopes. Again, the best performance was observed for the baseline cell and the worst for graphite. A high value for the resistance can be translated into a large performance loss since, for fuel cell operation, a resistive loss causes a decrease in the total cell voltage.

The heat stabilized Ru/Ir catalyst was chosen as the cathode catalyst for all subsequent experimentation. This catalyst was chosen because of its lower cost (as opposed to Pt and Pt/Ir), ease of preparation (as opposed to Ir), increased stability in a halide environment (as opposed to Pt) and improved performance (as opposed to graphite).

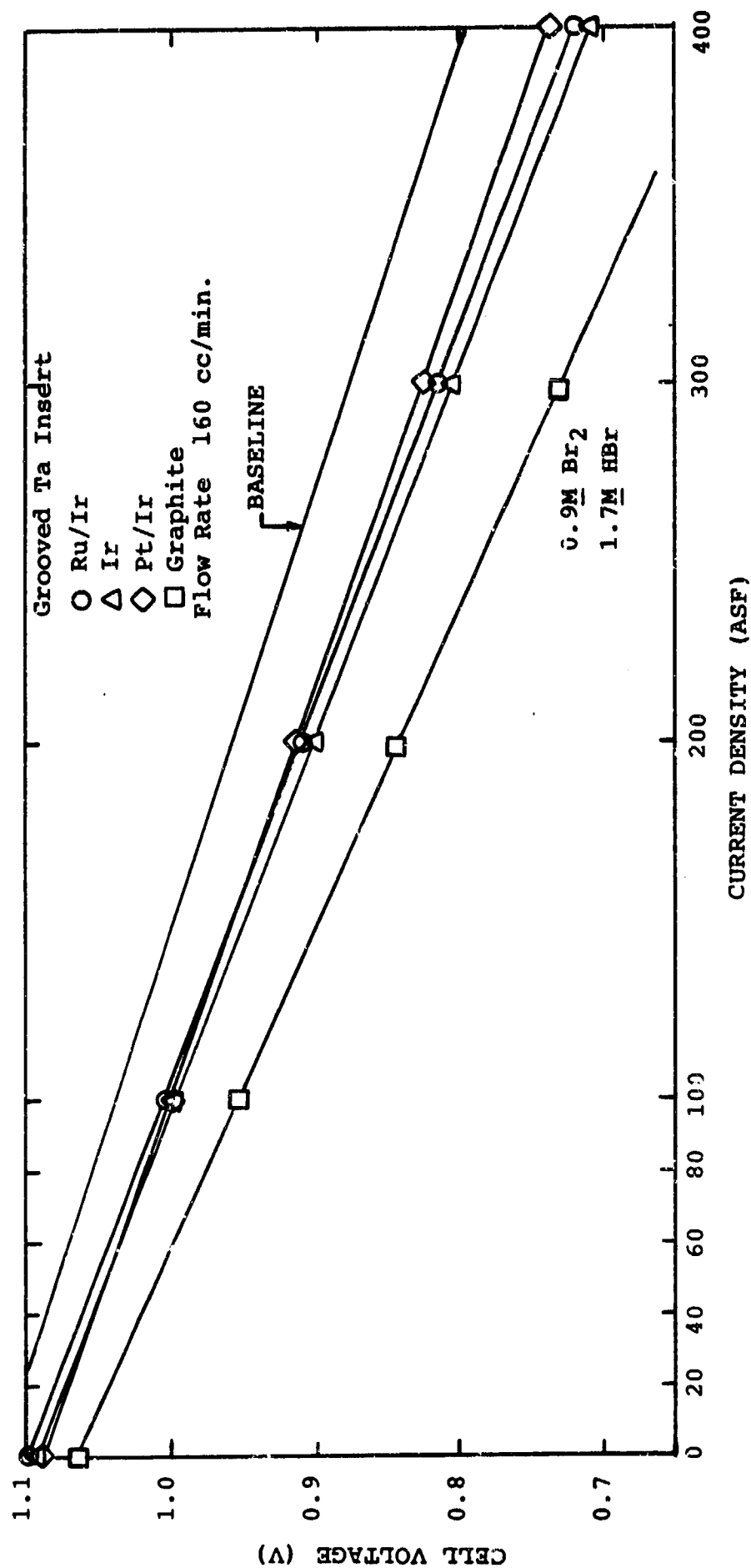


Figure 3. Effect of Cathode Catalyst

A series of experiments was run to characterize the fuel cell response as a function of bromine concentration at a fixed HBr concentration; these results are seen in Figure 4. At low bromine concentrations, the bromine was being consumed at the electrode surface much faster than it could be replaced by diffusion/mass transport. This was evidenced by the rapid drop in performance seen for 0.08M Br₂.

In an effort to improve the response of the fuel cell, especially at low bromine concentrations, the effect of liquid flow rate through the fuel cell was investigated, with the results being shown in Figure 5. To obtain the increased liquid flow rates through the fuel cell, the Ta flow field insert utilized in the baseline fuel cell was replaced with a reticulated vitreous carbon (RVC) insert. Figure 5 shows, for liquid flow rates above 340 cc/min, no increase in response was observed for an increase in liquid flow rate. This demonstrated the mass transport problems could be minimized with an increase in liquid flow rate.

Fuel cell response was also investigated as a function of HBr concentration; these results are shown in Figure 6. The bromine concentration was held constant in all cases. A decrease in performance was observed for each increase in acid concentration. This was due to:

- 1) A decrease in the reversible potential, E_{cell} with increasing acid concentration in accordance to the Nernst equation:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + RT/F \ln (\gamma^2 \text{HBr} C^2_{\text{HBr}} / a_{\text{H}_2}^{1/2} a_{\text{Br}_2}^{1/2})$$

where C and γ are the molality and activity coefficient for the acid.

- 2) An increase in solid polymer electrolyte resistance with increasing acid concentration. The decreasing solvent (H₂O) activity with increasing acid concentration dehydrates the membranes. This demonstrates the best performance was obtained for a fuel cell using 1M HBr as a supporting electrolyte.

A final experiment was performed to further increase performance of the fuel cell. Based on work performed with a hydrogen/chlorine fuel cell under GE funding, the RVC insert on the cathode side was replaced with a platinum clad niobium screen. Results of this experiment are shown in Figure 7. An increase in fuel cell performance was noted, with the increase amounting to 45 mV at 200 ASF; a similar increase was noted for the H₂/Cl₂ fuel cell. One potential drawback to use of the platinum clad niobium would be the dissolution of the Pt in the halide environment. It was anticipated that, in the presence of the PEG-Br₂ complex, this possibility would be minimized.

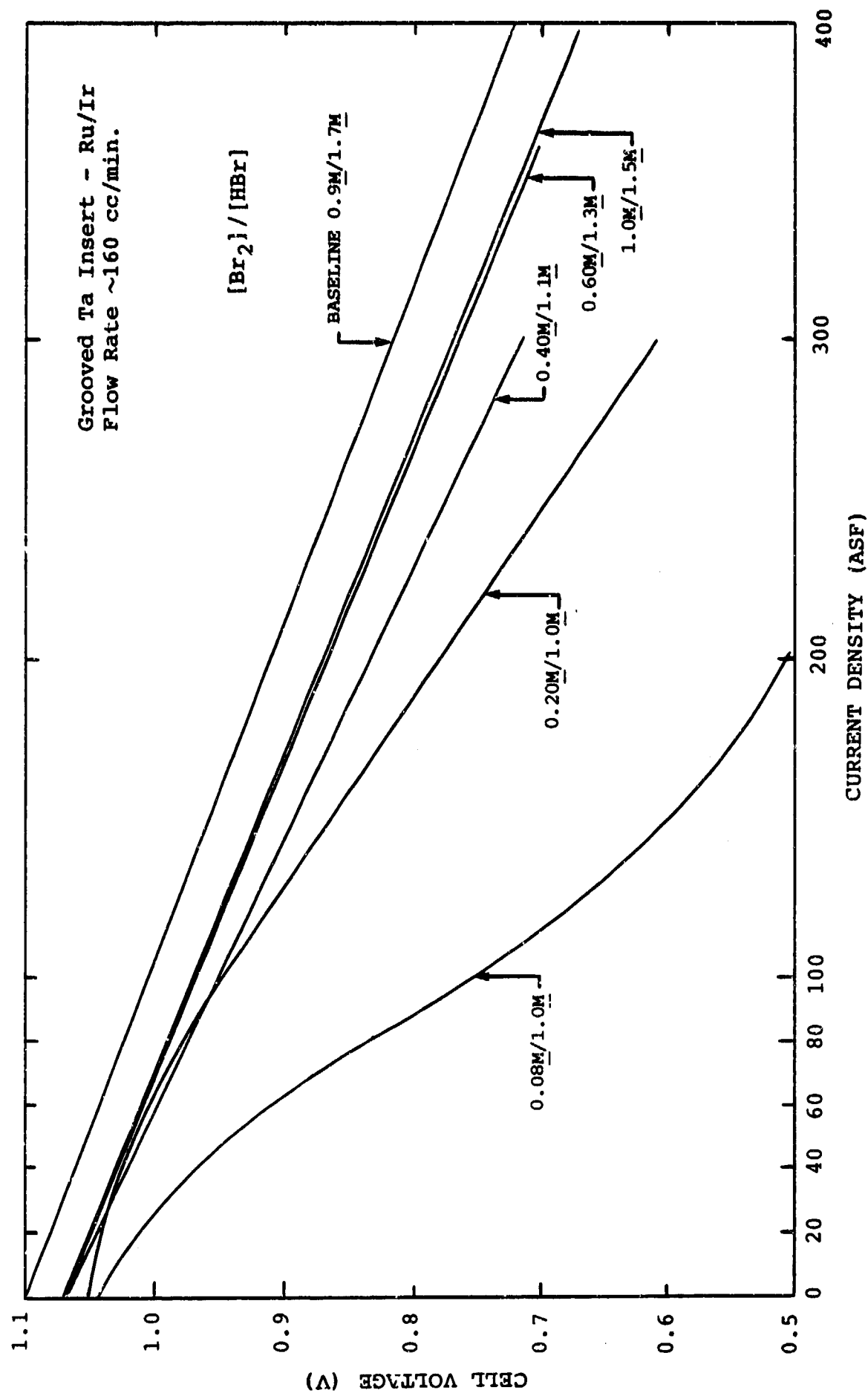


Figure 4. Fuel Cell Performance as a Function of Bromine Concentration

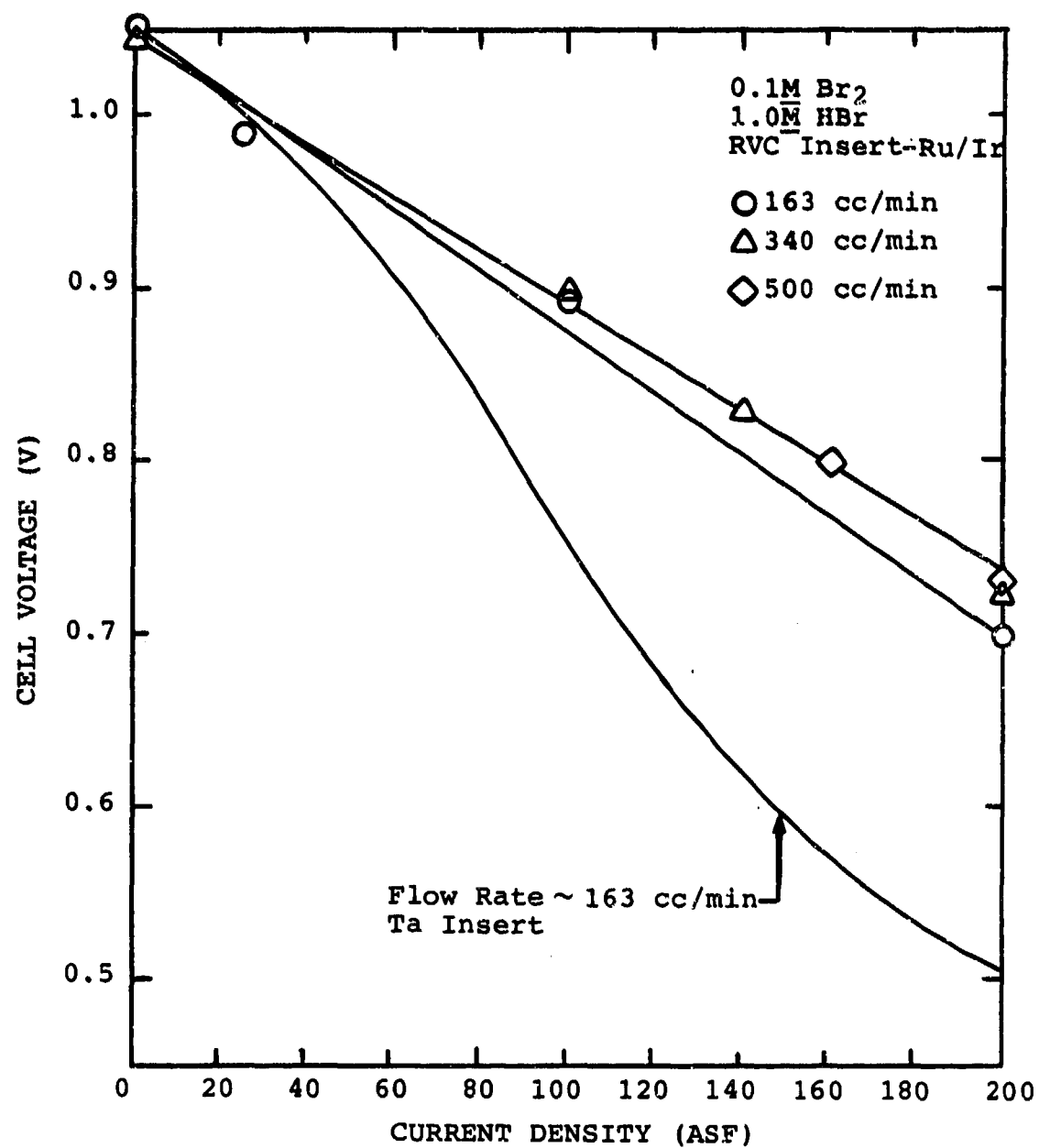


Figure 5. Effect of Flow Rate on Fuel Cell Performance

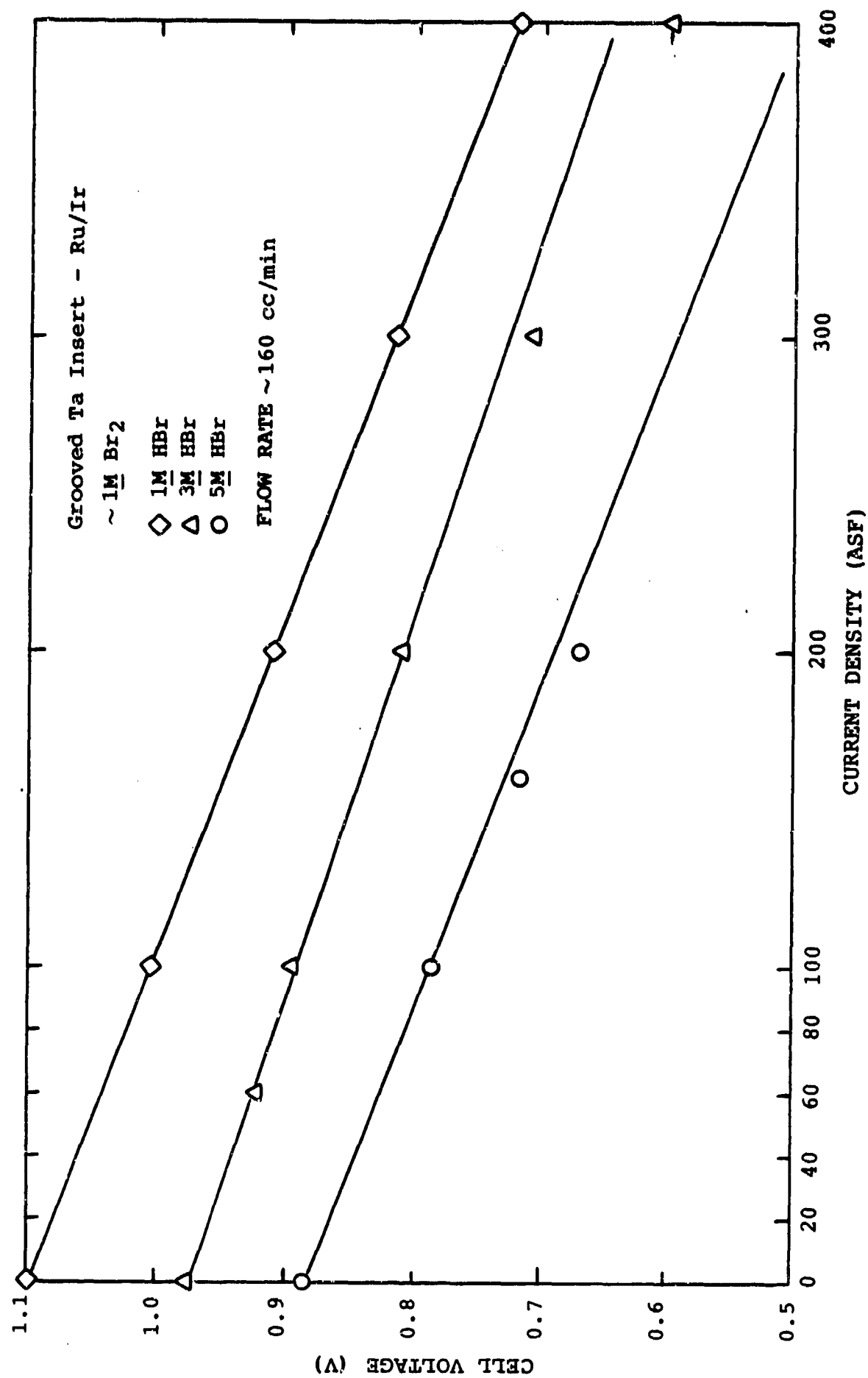


Figure 6. Effect of Acid Concentration

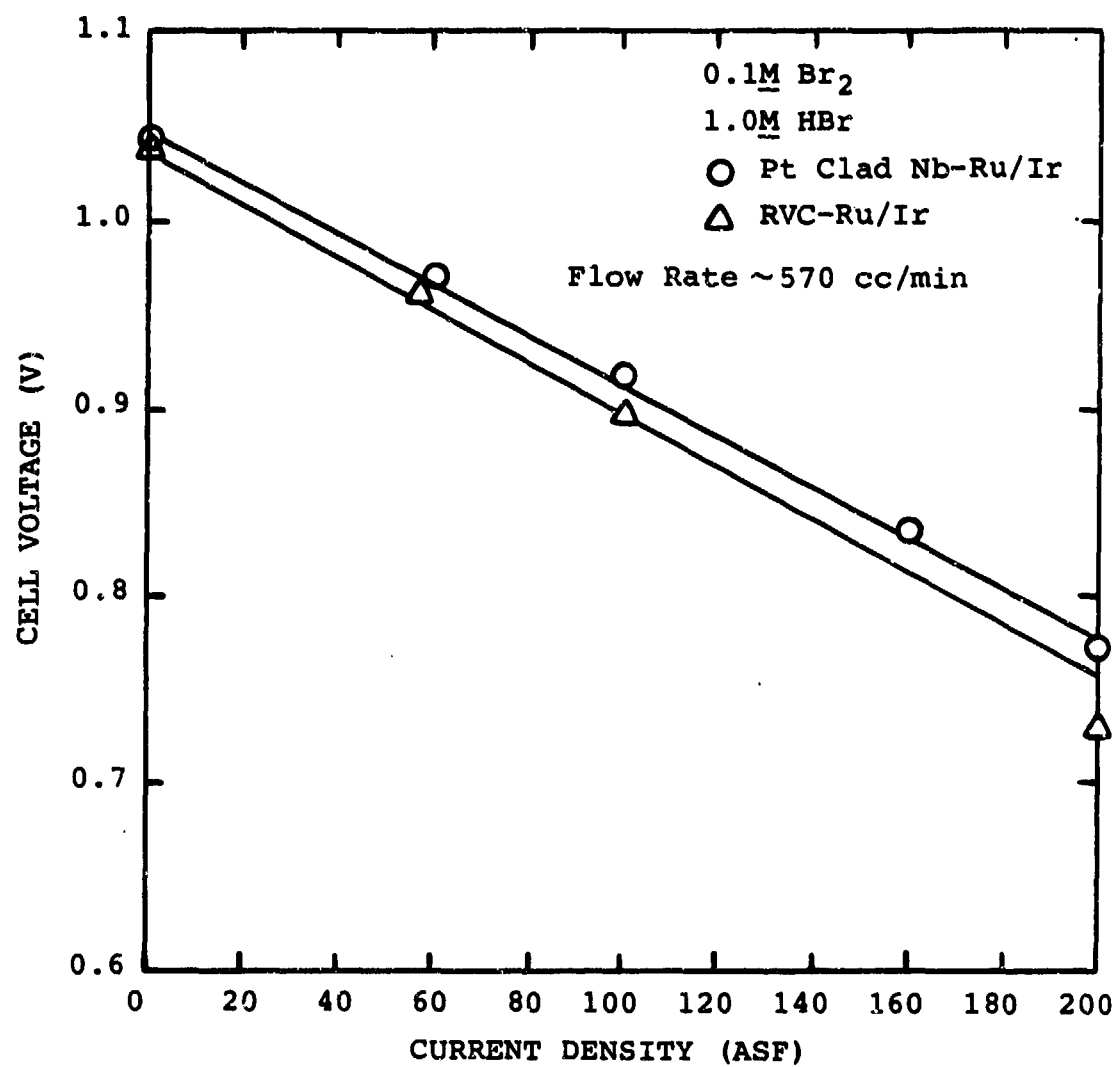


Figure 7. Cathode Current Collector Evaluation

The above experiments were conducted to optimize the H₂/Br₂ fuel cell. A summary of the optimized configuration is as follows:

Cathode Side (Bromine Electrode)

- Catalyst Ru/Ir
- Current Collector Pt clad Nb

Anode Side (Hydrogen Electrode)

- Catalyst Pt
- Current Collector Nb

Liquid Flow Rate >300 cc/min

Concentrations 1M Br₂/1M HBr

2.3 Cell Test Verification

The previous section describes experiments performed to develop an optimized bromine electrode for use in a hydrogen/bromine fuel cell. This fuel cell was subsequently evaluated using the PEG-Br₂ complex as a source of bromine.

The initial attempt at fuel cell operation using the PEG-Br₂ complex did not meet with success. Using 1M HBr as the reaction medium, a complex was formed using 0.5M Br₂ and 0.1M PEG. Over a 24/48-hour period, the oil formed fell out of solution and settled into low spots in the liquid circulation system; a flow rate of 575 cc/min was not enough to keep the complex circulating. Methods to keep the complex dispersed will be discussed later.

To keep the amount of oil formed in the system to a minimum, it was decided to operate with a low bromine concentration. Figure 8 shows the results obtained with 0.2M Br₂/1.2M HBr, using a Pt cathode catalyst. The system was then made 0.1M in PEG, and the resulting complex circulated through the fuel cell. Polarization data using the complex to supply bromine are also shown in Figure 8; a platinum clad niobium current collector was used in these experiments.

The complex was circulated for 3½ hours, bypassing the fuel cell, to allow for thorough mixing and complex formation. After this time, the complex was circulated back through the fuel cell and another polarization curve obtained; this is also seen in Figure 8. A drop in fuel cell performance was noted for each successive polarization curve.

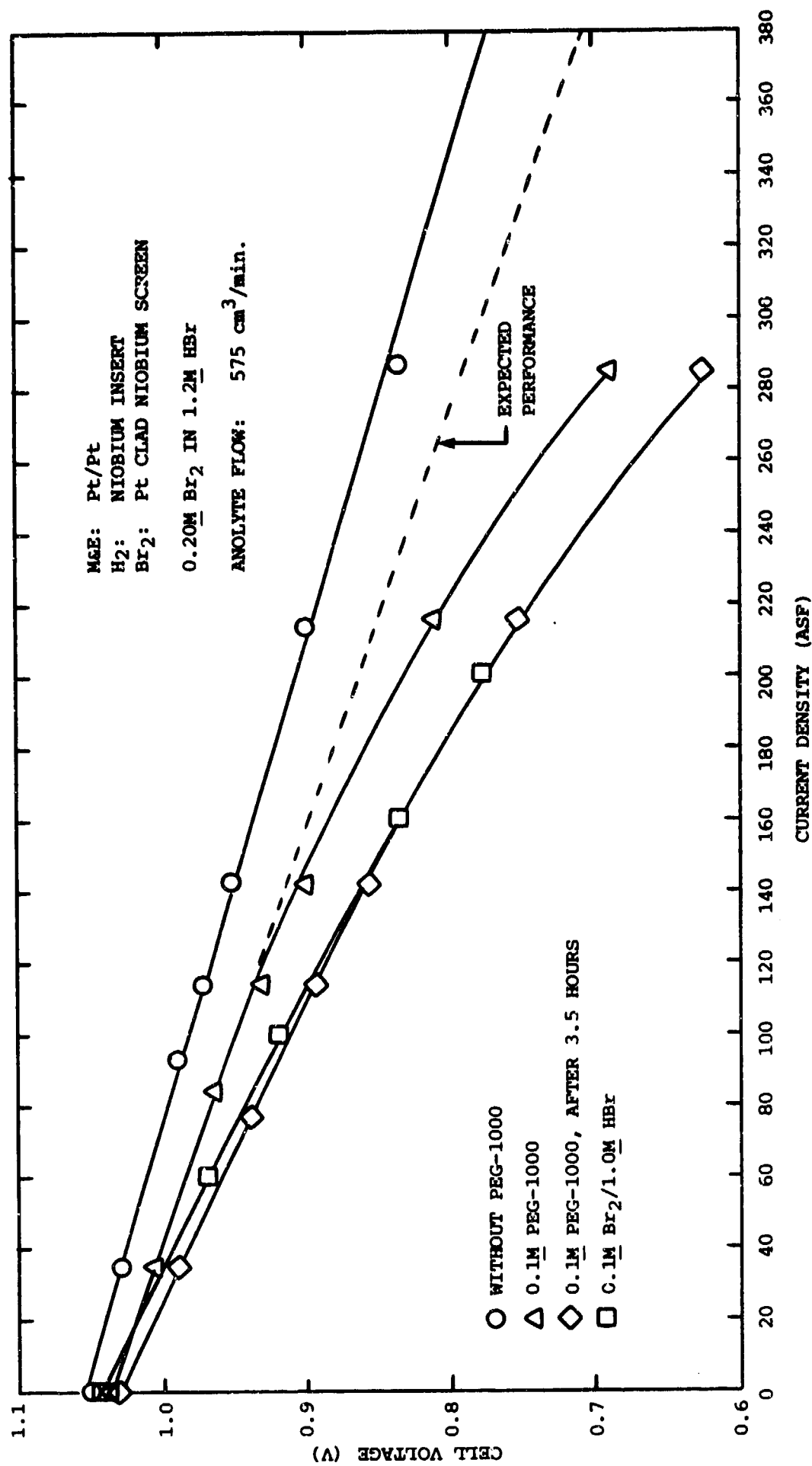


Figure 8. Fuel Cell Performance, With and Without PEG-1000 Present

The polarization curves in the presence of PEG both began to show a drop in response at current densities greater than 140 ASF. The shape of the curves indicated the fuel cells were operating in a bromine-depleted mode of operation. Analysis of the liquid phase passing through the fuel cell revealed an aqueous phase bromine concentration of 0.1M. Previous results have indicated an aqueous/oil phase ratio of 0.5 for Br₂/1M HBr in the presence of 0.1M PEG. Also shown in Figure 8 are results presented previously for a fuel cell containing a platinum-clad niobium screen operating with 0.1M Br₂/1M HBr. These results are almost identical to those obtained with the PEG-Br₂ complex, with an aqueous phase of 0.1M Br₂. It appears the fuel cell was responding only to uncomplexed Br₂. There was no apparent electrode reaction with the PEG-Br₂ complexed oil.

The Br₂/PEG/HBr mixture was circulated through the fuel cell for an ~72-hour period. During this time, the resistance of the fuel cell doubled. Due to the high resistance, another polarization curve was not obtained. Tear down of the fuel cell revealed a loss of the liquid bromine reduction cathode catalyst. Loss of the catalyst led to the rise in cell resistance. Investigation of the platinum-clad niobium by means of SEM/EDX analysis revealed the platinum was intact.

Evidently the activity of the uncomplexed 0.1M Br₂/1.2M HBr was sufficient to attack the high surface area platinum catalyst, but, over the short time frame of this experiment, had little effect on the smooth platinum of the platinum-clad niobium.

Similar experiments were run using a Ru/Ir cathode and both 1 and 3M HBr. These results are shown in Figures 9 and 10. Calculation of the IR-free cell voltage revealed the loss in performance between the initial and final PEG runs to be resistive in nature.

2.4 Surfactant Dispersing Agents/Alternative Complexing Agents

As mentioned in Section 2.3, the PEG-Br₂ complex accumulated in low spots in the liquid portion of the H₂/Br₂ fuel cell system. Several bench tests were performed in an effort to disperse the complex throughout the liquid portion of the system. These tests involved the use of surfactants to disperse the PEG-Br₂ complex. Four of the surfactants evaluated, which were Triton® surfactants, formed complexes of their own with bromine. It was later determined the Triton surfactants were based on a polyethylene glycol-type structure. Another surfactant evaluated was perfluoro-octanoic acid. This material did not form a bromine complex, but, under the conditions tested, was ineffective in dispersing the complex.

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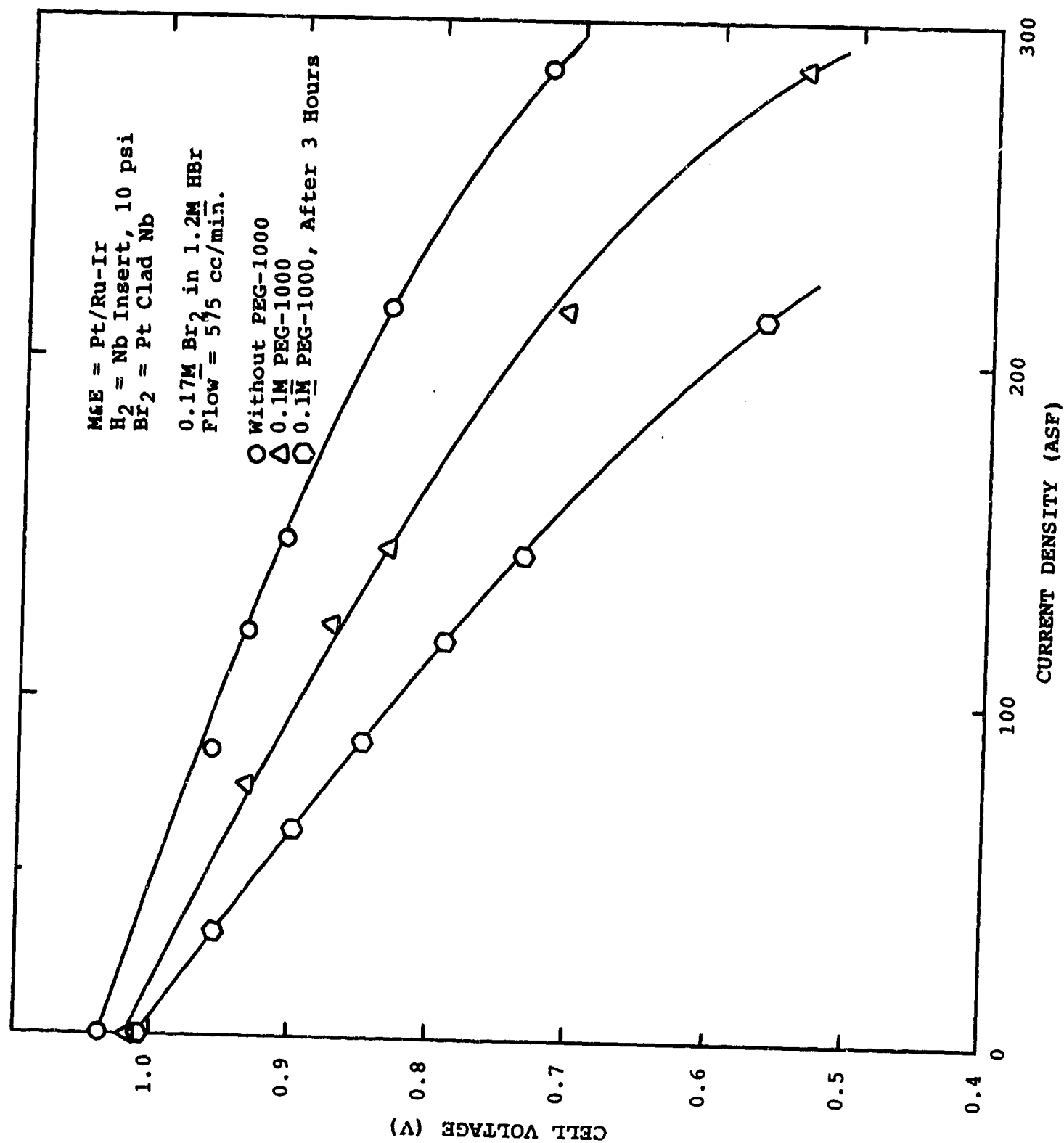


Figure 9. Fuel Cell Performance, Optimized Configuration, 1M HBr

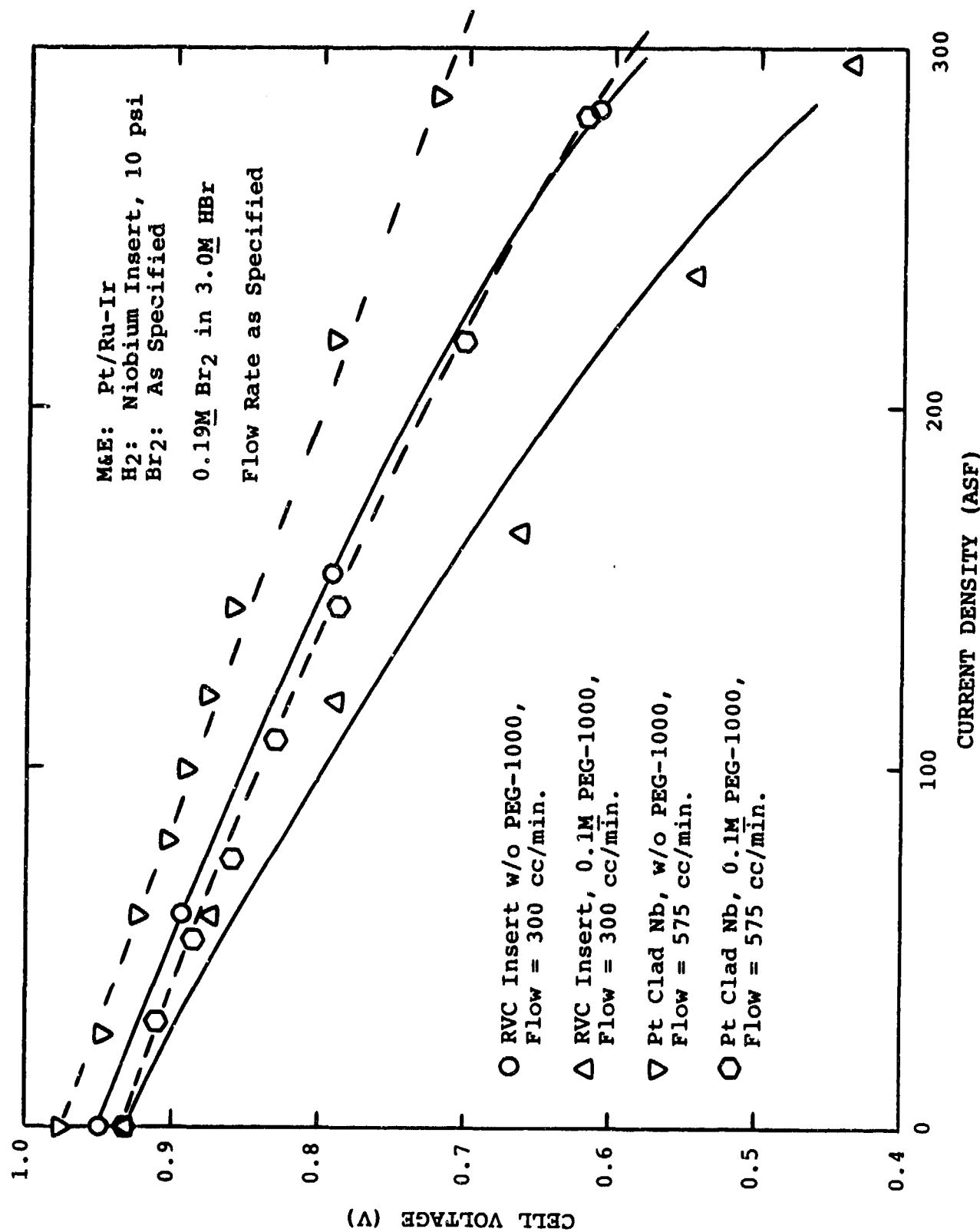


Figure 10. Fuel Cell Performance, 3M HBr

The other surfactants evaluated were Fluorad® surfactants. Of the three Fluorad surfactants, one was ineffective in dispersing the complex. The other two appeared to disperse the complex when agitated, but under stagnant conditions, the complex settled to the bottom of the test container. None of the surfactants were evaluated in the H₂/Br₂ fuel cell system.

The results presented in Section 2.3 of this report indicated the fuel cell was responding to uncomplexed bromine in solution; the complex evidently was not dissociating rapidly enough to supply the fuel cell with a sufficient quantity of bromine. Therefore, some initial experiments were conducted with an alternative complexing system.

The complexing agent evaluated, poly (vinyl pyrrolidone) was obtained in two different molecular weights, 10,000 and 40,000. The 10,000 molecular weight material will be referred to as PVP-10, while the 40,000 molecular weight as PVP-40. A potentiometric addition was performed using PVP-10 in 1M HBr; the results indicated 1 mmole of PVP-10 would absorb 13.3 mmoles Br₂. This compared with 1.95 mmoles Br₂ per mmole PEG-1000. In the case of the PVP-10, the complex formed was a fine yellow solid which was dispersed throughout the reaction kettle. This material settled when stirring was halted, and could be easily filtered. The (PVP-10)-Br₂ complex was readily soluble in cold water.

Two complexes were formed using a bulk addition method. The first complex was 5.9 mmoles of bromine added to 1.9 mmoles PVP-10 in 1M HBr while the second was 5.9 mmoles bromine added to 0.46 mmoles PVP-40. A yellow precipitate was formed in both cases. Analysis of the aqueous phase bromine content revealed a 54% decrease in bromine content over a nine-day period for the flask containing PVP-40 while almost no bromine was detected in the flask containing PVP-10. No precipitate was left in the PVP-10 flask. This demonstrated the PVP-Br₂ complexes were reversible and would release free bromine back to solution.

3.0 DISCUSSION

The data presented in Section 2.1, along with the data presented in the Interim Report (summarized in Appendix I) indicated the most desirable HBr acid concentration for the PEG(1000 MW)-Br₂ complex was 3M. The kinetics of complex dissociation were the most rapid for this acid concentration, the complex had a high bromine capacity, and the lowest thermal burden was placed on the system. Temperature data suggested operation as close to room temperature as possible.

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Based on fuel cell considerations only, the H_2/Br_2 system demonstrated the best performance using 1M HBr as a storage medium for liquid bromine. Operation at 3M HBr led to some loss in fuel cell performance due to 1) a decrease in HBr reversible cell voltage and 2) IR losses from membrane dehydration.

Overall system performance for the $H_2/PEG-Br_2$ fuel cell was evaluated in both 1 and 3M HBr. A more linear performance plot was observed for 3M HBr, with only a 15 mV polarization loss at 200 ASF. Compared to baseline performance, polarization losses were 110 and 125 mV in 1 and 3M HBr, at 200 ASF, respectively.

The data presented in Section 2.3 indicated the fuel cell was responding to free, uncomplexed bromine in solution. Evidently the rate of dissociation of the $PEG-Br_2$ complex was not sufficiently rapid for the complex to supply bromine directly to the cathode surface. The $PEG-Br_2$ complex can be utilized, however, as a bromine storage medium, because the presence of PEG will allow a large inventory of bromine to be stored safely under reduced halogen vapor pressure.

During the interim period between Phase I and Phases II/III of this program, work performed under General Electric funding demonstrated that, for a given bromine concentration, increasing the PEG concentration would lead to a decrease in aqueous phase bromine concentrations. In 5M HBr, it was possible to reach 0.4M PEG; typical PEG concentrations used under MERADCOM funding have been on the order of 0.1M. Results from Phase I demonstrated that holding the PEG concentration constant and increasing the bromine concentration led to an increase in the uncomplexed bromine concentration. Therefore, making use of these factors, through proper choice of both the PEG and Br_2 concentrations, a system could be set up in which the uncomplexed bromine concentration would be high enough for efficient fuel cell operation, but low enough for safety and materials considerations. Simultaneously, the concentration of complexed bromine could be made large enough to store sufficient bromine for extended fuel cell operation.

An area of concern which requires further investigation is the use of surfactant dispersing agents to effectively disperse the complex throughout the liquid phase of the system. At the present time, a complex made by reacting 0.1M PEG with 0.5M Br_2 , will accumulate in low areas in the liquid flow system, even at high liquid flow rates. Preliminary results have indicated two surfactants which show potential for use in this area. Further investigations are needed to determine the effect of complex dispersal throughout the liquid flow system and the effect of the surfactant on the fuel cell response.

Finally, preliminary data was obtained on the use of alternative complexing agents. Complexes formed with poly (vinyl pyrrolidone) have been shown to have a higher bromine content than PEG complexes (due to the higher molecular weight of the PVP). This complex has also demonstrated the ability to release bromine back to solution. Considerable characterization is required, however, before the PVP complexes can be considered for use.

4.0 RECOMMENDATIONS

Based on the experimental work performed under this program, the following recommendations are made:

- Short-term testing has indicated the Ru-Ir cathode catalyst is stable in the HBr-PEG-Br₂ environment. Long-term testing is required to verify this stability.
- Short-term testing has indicated the Pt Black anode catalyst has to be maintained at hydrogen potentials to avoid dissolution or poisoning by the permeating HBr/Br₂ anolyte solution. A more stable hydrogen anode catalyst system is required that has improved tolerance to the anolyte.
- Several surfactants have demonstrated the potential for dispersing the PEG-Br₂ complex throughout the liquid phase. Further testing is required to determine the effect of surfactants on the fuel cell response, and to verify the ability to disperse the complex in the H₂/Br₂ fuel cell apparatus.
- Alternative complexing agents such as those based on poly (vinyl pyrrolidone) have demonstrated potential for useage. Extensive evaluation is required before their use can be recommended.
- Mass transfer studies indicate a Pt Clad Nb used with the Ru-Ir bromine anode catalyst leads to improved performance. Alternate noble metal-coated collectors/ electrodes (Ru, Ir Coated RVC, meshes) used in an optimized design are required to maximize electrode reaction rate and fluid transfer.

5.0

REFERENCES

1. F. G. Will, U.S. Patent No. 4,058,650 (1977).
2. E. N. Balko, General Electric Co., Internal Memo Report (1982).
3. Interim Report, MERADCOM Contract No. DAAK-70-82-C-0088, (June 1983).
4. E. N. Balko, J. Applied Electrochemistry, 11 (1981) 91.
5. O. Hassel and J. Hvoslef, Acta. Chim. Scand., 8, (1954) 873.
6. P. Groth and O. Hassel, Acta. Chim. Scand., 18 (1964) 402.

6.0

APPENDIX I - SUMMARY OF PHASE I RESULTS

This section summarizes results obtained during Phase I of the program, which show the effect of acid concentration and temperature on the PEG-Br₂ complex. Heats of formation for the complex were also measured.

6.1

Concentration and Temperature Effects

Hydrobromic acid is utilized in the H₂/Br₂ regenerative fuel cell system as both a reactant and a reaction medium. As seen in Figure 1, the HBr is electrolyzed to H₂ and Br₂. In the fuel cell mode, HBr is a product of the cathode reaction. In the Br₂ storage system, HBr is used as a reaction medium throughout which the PEG-Br₂ complex is dispersed. Preliminary investigations at GE/EECP demonstrated the PEG-Br₂ complex was soluble in 10 M HBr, thus to maintain a two-phase system this high acid concentration must be avoided. The effect of varying HBr concentration on PEG-Br₂ complex formation was studied over the range 1 to 7 M HBr. Acid concentrations above 7 M HBr will tend to dehydrate the ion-exchange membrane used as the electrolyte in the electrolysis and fuel cell leading to increased membrane resistance (4). Therefore, acid concentrations were kept below 7 M.

Table A-I presents results obtained by use of a potentiometric addition technique. Potentiometric addition was used to screen the initial formation of a PEG-Br₂ complex. With this technique, a known amount of Br₂/HBr was added dropwise to a thermostated reaction kettle containing either HBr only (blank) or PEG dissolved in HBr. The potential of the resulting solution was monitored with respect to a Ag/AgBr reference electrode. Results obtained in a typical potentiometric addition are shown in Figure A-1. In the absence of PEG, the resulting line followed a Nernst-type response with a slope of 30-34 mV/decade. With glycol present, a plateau was visible in the plot. This plateau corresponded to the formation of a visible, second phase in solution. The Br₂/PEG mole ratio increased with increasing HBr concentration as shown in Figure A-2 and Table A-I.

TABLE A-I
POTENTIOMETRIC ADDITION DATA

<u>HBr Conc.</u> <u>(M)</u>	<u>Br₂ Conc.</u> <u>(M)</u>	<u>PEG Conc.</u> <u>mM</u>	<u>Mole Ratio,</u> <u>Br₂/PEG</u>
1.0	1.15	20.046	1.95
2.8	1.64	20.022	2.38
5.1	1.65	20.052	2.63
6.9	1.60	20.023	3.21

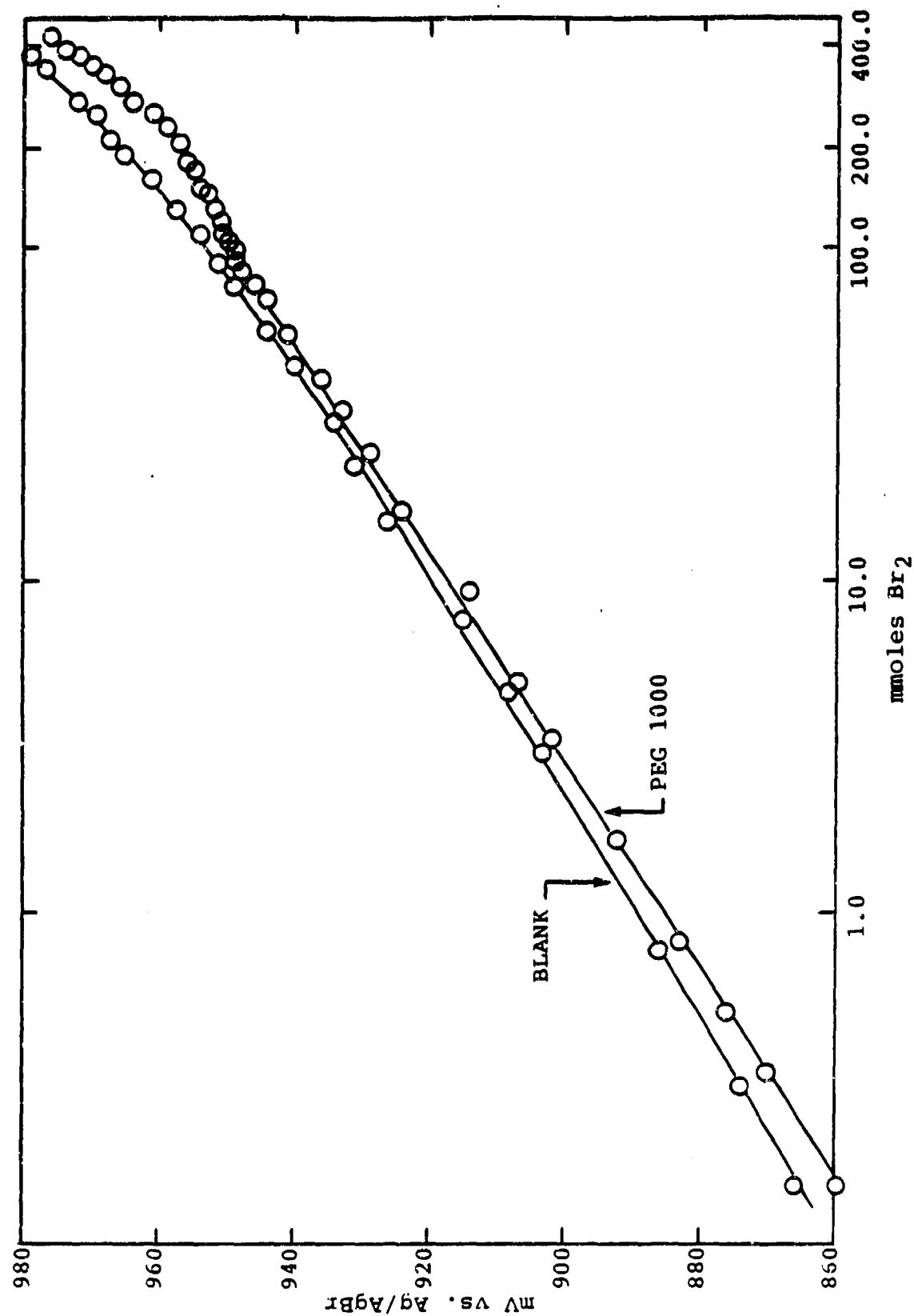


Figure A-1. Typical Potentiometric Addition Curve

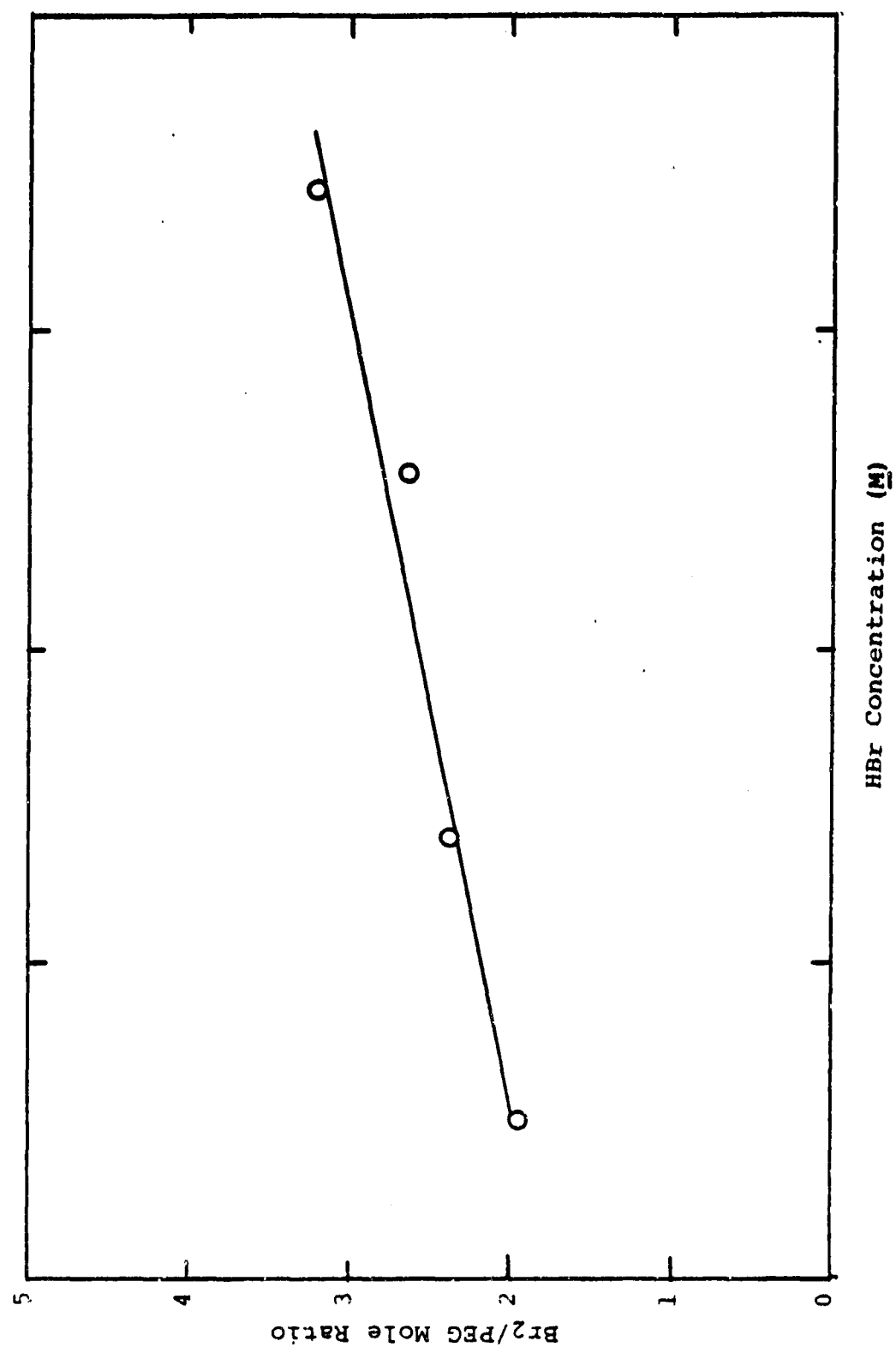


Figure A-2. Variation of Br₂/PEG Mole Ratio with HBr Concentration

Table A-II and Figure A-3 provide similar results for complexes prepared by a bulk addition method. In this method, Br₂/HBr was added rapidly to a mixture of PEG/HBr, the resultant mixture agitated for 24 hours, and then allowed to sit quietly for a 45 day period. Similar results were observed for both potentiometric and bulk additions, with the Br₂ content of the oil increasing as the HBr concentration was increased. In the case of the bulk addition oils, the aqueous phase Br₂ content was also determined. These results, also shown in Figure A-3, follow the same general trend as the complex phase bromine content.

The stability of complexes formed by the bulk addition method was studied as a function of time. Complexes were prepared by addition of 100 mmols Br₂ to 1, 3, 5, and 7 M HBr, with each acid concentration containing 20 mmols PEG. The resulting solutions were agitated for 72 hours. One week later, the aqueous and oil phases were separated and analyzed for bromine content. Fifty-five days after separation, the oil and aqueous phase were again analyzed for bromine content. Except for the 1 M HBr aqueous phase, which showed a 19% decrease in bromine content, all results were within $\pm 5\%$ of the original bromine content.

The non-separated oil and aqueous phases were also analyzed for bromine content after a sixty-two day period. The oil phase bromine content had an average decrease of 3.1% while the aqueous phase bromine content increased an average of 2.6%. This indicated the partition coefficient of the complex might have changed slightly over a two month period in which samples were allowed to remain stagnant.

Bulk addition experiments using 5 and 7 M HBr to study the effect of high bromine concentrations on complex formation are summarized in Table A-III. To study this effect, 500 mmols of bromine were added to 20 mmols of PEG-1000 dissolved in HBr, and the resulting aqueous and oil phases analyzed for bromine content. These results are compared with those from a similar experiment involving only 180 mmols of bromine. The data in the last two columns of Table A-III are particularly noteworthy because they show that PEG-1000 will absorb only a specific amount of bromine from a Br₂/HBr solution and that any excess bromine will remain in solution. This implies that the total bromine concentration must be limited to maximize the percentage of complexed bromine while minimizing the amount of uncomplexed (free) bromine in solution.

The bulk addition samples whose bromine concentrations were presented in Table A-III were also analyzed for bromide ion content. Table A-IV lists the results of these analyses. The second column is the total mmols of Br⁻ expected in the sample. This is found by considering the initial amount of Br₂ added (180 mmols Br₂ = 360 mmols Br⁻) plus the concentration of the HBr used as the reaction medium. The third column is the total

TABLE A-II
RESULTS OF OIL ANALYSIS - BULK ADDITION

<u>HBr</u> <u>CONC.</u> <u>(M)</u>	<u>MMOLES Br₂</u> <u>OIL PHASE</u>	<u>MMOLES Br₂</u> <u>AQUEOUS PHASE</u>	<u>TOTAL</u> <u>MMOLES Br₂</u>	<u>AQUEOUS PHASE/</u> <u>OIL PHASE</u>	<u>OIL DEN-</u> <u>SITY (g/ml)</u>
1	87.4	40.2	127.6	0.46	1.522
3	107.8	73.2	181.0	0.68	1.603
5	110.4	71.1	181.5	0.64	1.629
7	116.6	76.5	193.1	0.66	1.674

TABLE A-III
RESULTS OF OIL ANALYSIS

<u>HBr</u> <u>CONC</u> <u>(M)</u>	<u>MMOLES Br₂</u> <u>OIL PHASE</u>	<u>MMOLES Br₂</u> <u>AQUEOUS PHASE</u>	<u>(AQUEOUS PHASE)</u> <u>OIL PHASE</u> <u>500 MMOLE</u>	<u>(AQUEOUS PHASE)</u> <u>OIL PHASE</u> <u>180 MMOLE</u>
5	175.7	313.4	1.78	0.64
7	176.2	299.4	1.70	0.66

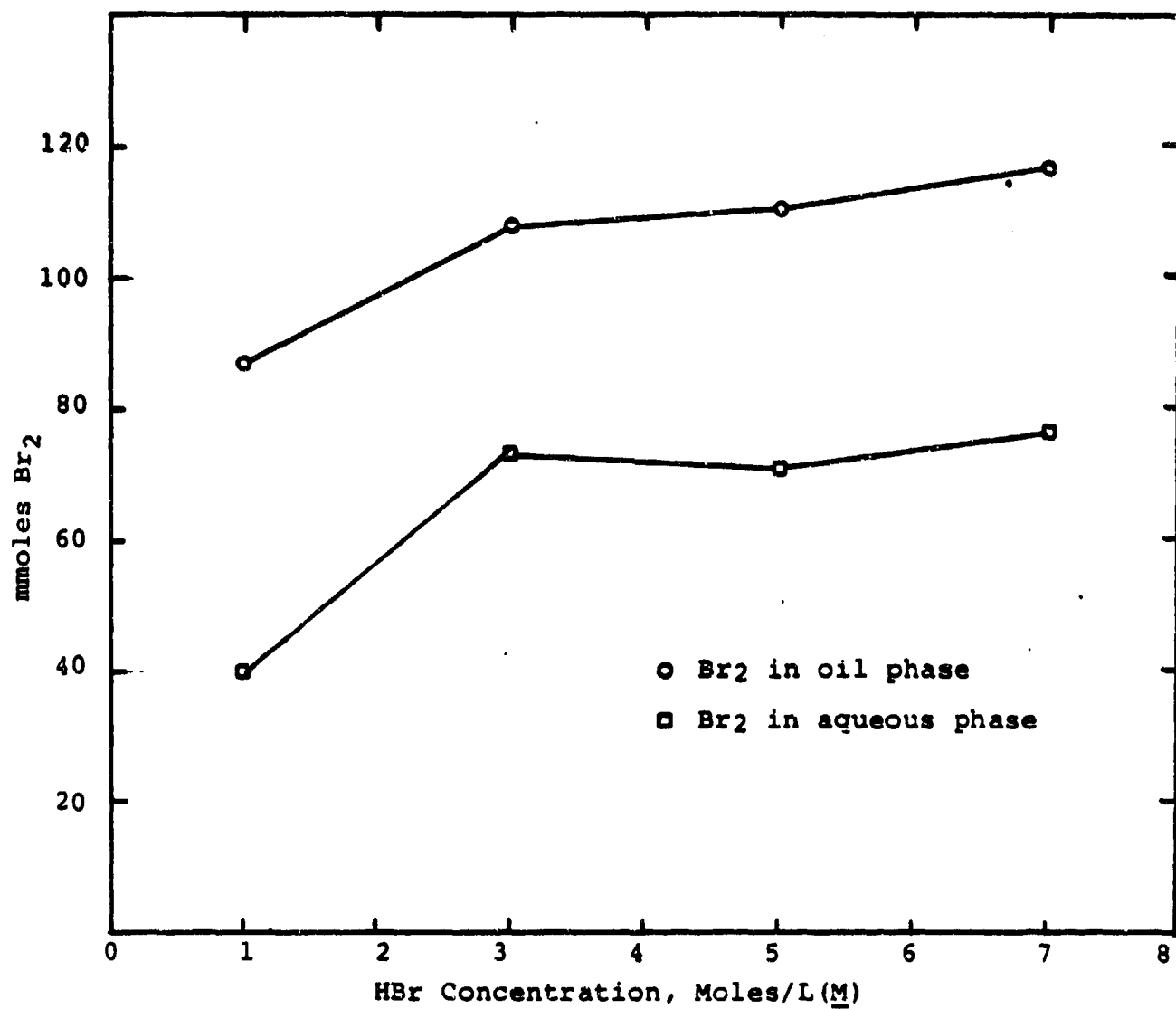


Figure A-3. Br₂ Content as a Function of HBr Concentration

TABLE A-IV

BROMIDE ION ANALYSIS RESULTS - BULK ADDITION

<u>HBr Conc (M)</u>	<u>Total mmoles Br⁻ Expected</u>	<u>Total mmoles Br⁻ Measured</u>	<u>Total mmoles Br⁻</u>		<u>(mmoles Br₂ Excess Br⁻) Oil Phase</u>
			<u>Aqueous Phase</u>	<u>Oil Phase</u>	
1	660	610.9	384.0	227.9	1.65
3	1260	1292.7	1020.0	272.7	1.89
5	1860	1753.4	1470.0	283.4	1.76
7	2460	2452.3	2130.0	322.3	1.31

Br⁻ content found in both the aqueous and oil phases, while the next two columns divide the total Br⁻ content between the aqueous and oil phase contents. Finally, the last column is the ratio of oil-phase Br₂ content to the excess Br⁻ found in the oil phase. Excess Br⁻ content is defined as the difference between the total oil phase Br⁻ content and the oil phase Br₂ content, expressed as Br⁻.

An analysis of the data presented in Table A-IV indicates that the total Br⁻ content for each acid concentration is within 10% of the expected Br⁻ concentration. Part of the error is due to loss of Br₂ through volatilization. Also, the HBr concentrations were not determined by titration prior to the experiment, which would account for some of the differences between the "expected" and measured Br⁻ content.

The last column of Table A-IV is useful in elucidating the structure of the complex oil. Single crystal X-ray measurements (5) have been made of the solid compound formed by the cyclic polyether 1,4 dioxane and bromine. In this material, bromine molecules formed a bridge between oxygen atoms in adjacent molecules. Such bridging also exists in bromine-methanol and bromine-acetone complexes. Infra-red spectroscopy (2) of complexes formed from different molecular weight glycols are similar to those of bromine complexes formed with single ethers.

The data from Table A-IV suggest, for the 1, 3 and 5 M acids, the average ratio of Br₂ to excess Br⁻ is 1.77. That is, there are approximately 2 moles of bromine present in the complex for each mole of Br⁻. A possible structure for the PEG-Br₂ complex is shown in Figure A-4. The negative charge on the tribromide ion is probably balanced by a hydrogen ion from the HBr. Also, cross-linking of polymers can occur as well as bridging between alcoholic and etherial oxygen atoms.

The effect of temperature on complex formation was also examined by potentiometric addition at 25, 35, and 45°C with 5 M HBr as a reaction medium. The shape of the potentiometric addition plot changed as the temperature was increased, the most noteworthy change being the disappearance of the plateau. After addition had been completed, the reaction kettle was held at temperature for approximately 18 hours after which time the resulting oils were collected and subsequently analyzed for bromine content. Results are in Table A-V.

The data in Table A-V shows a definite decrease in the amount of bromine taken up by the oils as the temperature increases. A similar trend has been observed in 1 M HBr. It was suggested previously that the O-Br bond energy in a methanol-bromine addition compound is roughly comparable to a strong hydrogen bond (6). A similar assumption has been made here for

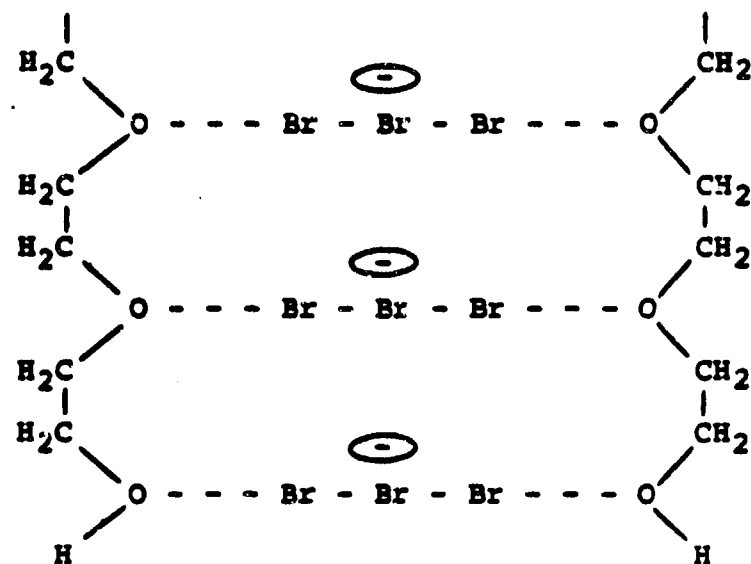


Figure A-4. Proposed Structure for Complex

TABLE A-V

EFFECT OF TEMPERATURE ON PEG-Br₂ COMPLEX

<u>Formation Temperature (°C)</u>	<u>mg Br₂/g Complex</u>
25	411.8
35	399.0
45	387.3

the PEG-Br₂ complex. Evidently as the temperature increases, the bond energy is not large enough to hold the complex together, and lesser quantities of bromine are absorbed. Analysis of the aqueous phase of these solutions (25, 35, and 45°C) showed the bromine concentration was essentially constant indicating that the bromine was being lost from the PEG phase as a vapor, which was usually apparent above the solution.

6.2 Thermodynamic Studies

Studies were performed to measure the heat of formation for the PEG-Br₂ complex. This information is required so that proper heating or cooling can be designed into the regenerative fuel cell system.

Thermodynamic studies were performed using a glass-lined calorimeter. Known volumes of Br₂/HBr mixtures were added to either HBr only, or to a PEG/HBr mixture. The former experiment allowed heats of dilution to be calculated, while the latter gave values for the heats of formation. Heat capacities were measured for each experiment by means of an immersion heater/stirrer assembly.

Results of the experiments are summarized in Table A-VI; heats of formation are listed in column 3 and heats of dilution are listed in column 4.

Column 2 lists the amount of bromine added in each experiment. Two experiments were run using 0.9 M HBr. In one case, 71 mmoles of Br₂ were used whereas in the other 142 mmoles of Br₂ were used. Heats of formation for the two experiments were identical. A difference, however, was noted in the heat of dilution.

The heats of formation and dilution are the same order of magnitude, and appear to show a minimum in the 3-5 M HBr range. To measure the heats of dilution and formation, known volumes of Br₂/HBr mixtures were added to either a known volume of HBr alone, or an HBr-PEG mixture, and the ensuing heat loss measured. Therefore, a heat of dilution was present in all experiments. In an actual operating electrolyzer (where the PEG-Br₂ complex will be formed), the large volume change associated with the calorimeter and current experimental system will not be present, minimizing the heat of dilution. The last column of Table A-VI gives the net measured heat for each system. This states the overall system will absorb a small amount of heat, with the smallest amount occurring in the 3-5 M HBr range.

6.3 Discussion

The data in Section 6.0 (Appendix) identify some trends which will be useful in establishing operating conditions for a regenerative fuel cell system utilizing the polyethylene glycol-bromine storage system. As evidenced in Figure A-3, the Br₂/PEG mole ratio increases as the HBr concentration increases. Stated another way, the higher the HBr concentration, the greater the amount of bromine absorbed by the complex. This trend was observed in both potentiometric additions and bulk addition studies in which the bromine concentration was held constant. Therefore,

TABLE A-VI

MEASURED HEATS OF FORMATION AND DILUTION

<u>HBr CONC (M)</u>	<u>mmoles Br₂ ADDED</u>	<u>ΔH FORMATION (Kcal/MOLE)</u>	<u>ΔH DILUTION (Kcal/MOLF)</u>	<u>NET HEAT (Kcal/MOLE)</u>
0.9	142	6.6	5.0	+1.6
0.9	71	6.6	7.1	-0.5
2.7	102	2.7	3.0	-0.3
4.7	112	4.3	4.6	-0.3
7.0	150	4.4	3.2	+1.2

based on HBr concentration alone, the system should be run over the range 3 to 7 M HBr to take advantage of the larger bromine capacity of the complex.

Temperature considerations suggest operation of the regenerative system as close to ambient temperature as possible. As the temperature is increased, the complex will release Br₂ above the solution, posing an increased threat to personal hygiene in the event of a system failure and liquid inventory spill.

The thermodynamic data in Section 6.2 suggest operation of the system using 3-5 M HBr as a reaction medium. These concentrations have been found to liberate the smallest amount of waste heat and will place the smallest thermal burden on the system.

In summary, the results indicate the most desirable HBr acid concentration acid range for the PEG (1000 MW)-Br₂ complex is 3 to 5 M with a possible useful range of 3 to 7 M. The most desirable operating temperature with this complex is 25°C.